DEPARTMENT
OF
CHEMICAL ENGINEERING

SRM UNIVERSITY, KATTANKULATHUR
KANCHEEPURAM DISTRICT, TAMILNADU – 603203

15CH207J
PHYSICAL AND ANALYTICAL CHEMISTRY LABORATORY

SEMESTER IV

NAME:

REG.NO:

SRM UNIVERSITY

(Under Section 3 of UGC Act, 1956)
SRM Nagar, KATTANKULATHUR – 603203
KANCHEEPURAM DISTRICT

BONAFIDE CERTIFICATE

Register No: ________________________

Certified to be the bonafide record of work done by__________________________ of ________________________________ B.Tech Degree course in the practical ______________________________________ in **SRM University, Kattankulathur** during the academic year ____________________

Lab Incharge

Date:

Head of the Department

Submitted for University examination held in ______________________________
SRM University, Kattankulathur.

Date **Examiner I** **Examiner II**

Name: **Branch:**

Reg. No:

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EXPERIMENT NO. **DATE:**

DETERMINATION OF CRITICAL SOLUTION TEMPERATURE FOR PHENOL - WATER SYSTEM

AIM:

To determine the critical solution temperature for phenol water system and to find out the percentage of phenol in the given sample.

APPARATUS:

Burette, boiling tube, thermometer, water bath etc.

THEORY:

Phenol and water are partially miscible at ordinary temperatures. Therefore, on shaking these two liquids with each other, two saturated solutions of different compositions, one of phenol in water and the other of water in phenol, are obtained. Such solutions of different compositions co-existing with one another are termed conjugate solutions. The mutual solubility of phenol and water increases with rise in temperature and, therefore, the concentration of phenol in water as well as that of water in phenol goes on increasing with rise of temperature and ultimately at a certain temperature the two conjugate solutions change into one homogeneous solution. This temperature is known as consolute temperature or critical solution temperature.

PROCEDURE:

Take a clean dry boiling tube, fit it with a thermometer and a stirrer, and clamp it vertically to a clamp stand. Place 5.0 ml of phenol into the boiling tube. Add 3.0 ml of distilled water through burette and mix well. Dip the tube into a transparent water bath and slowly heat the mixture with constant stirring. Note the temperature at which the turbidity, of the mixture, just disappears to become a clear solution. Remove the boiling tube from the heat and cool the mixture slowly with constant stirring. Note the temperature at which the turbidity reappears. Add another 2.0 ml aliquot of water to the mixture and repeat the above procedure (steps 4 to 7), i.e., Repeat the procedure (steps 4 to 7) after every addition of 2ml increments of water up to a final volume of about 28.0 ml of water. Carry out the above procedure with the given sample and note down the temperature.

Plot a graph between temperature and volume percentage of phenol.

DETERMINATION OF CRITICAL SOLUTION TEMPERATURE

OBSERVATION:

S. No.	Vol. of phenol taken (ml)	Vol.(V_1) of water added (ml)	Vol. percentage of phenol $= \left(\frac{5}{5+v_1}\right)100$	Temp. of disappear- -ance of turbidity (°C)	Temp. of appearance of turbidity (°C)	Mean Temp. (˚C)
1	5	3				
2	5	5				
3	5	7				
4	5	9				
5	5	11				
6	5	13				
7	5	15				
8	5	17				
9	5	19				
10	5	21				
11	5	23				
12	5	25				
13	5	27				`
14	5	29				
15	5	31				
16	unknown sample					

Plot a graph between mean temperature against volume percentage of phenol.

From the graph

- Critical Solution Temperature = --------------°C
- Critical solution composition = ---------------% by volume of phenol.
- Amount of phenol in the given sample = -----------%

RESULT:

- The CST of phenol water system was found to be ______ ºC.
- The critical solution composition was found to be _____% by volume of phenol.
- The percentage of phenol in the given sample was found to be _____%volume.

Internal Assessment:

Observation(5)	
Calculations, graph, result(10)	
Viva(5)	

EXPERIMENT NO. **DATE:**

CONDUCTOMETRIC TITRATION

AIM:

To find out the strength of hydrochloric acid and acetic acid in a given mixture by titrating it against sodium hydroxide solution, conductometrically.

APPARATUS:

Conductivity meter, burette, pipette, beakers, volumetric flask, etc.

THEORY:

Current is conducted through an electrolytic solutions by the movement of positive and negative ions in opposite directions. The conductance of a solution is proportional to the number of ions, the charge of each ion and ionic speed. Conductance of any solution is generally expressed as equivalent conductance (mS). It is defined as the conductivity of all the ions produced by 1 g equivalent of the electrolyte in a given volume of solution.

When a strong acid such as HCl is titrated against strong base such as NaOH, the following reaction taking place is

$$HCl + NaOH \text{ ----------------> } Na^+Cl^- + H_2O$$

During the course of the titration, the fastest moving H^+ ions are replaced by the less mobile Na^+ ions. Hence, the conductivity decreases rapidly. At the equivalence point, all the H^+ ions are neutralized. When excess of NaOH is added it introduces the fast moving OH^- ions and then the conductivity again increases. So two straight lines meeting at the minimum point is obtained in the plot of conductance against volume of NaOH solution. The volume of NaOH corresponding to the minimum point is the titre value.

When a weak acid like acetic acid is titrated against a strong base such as NaOH, the following reaction takes place

$$CH_3COOH + NaOH \text{ ------------> } CH_3COONa + H_2O$$

Acetic acid is partially ionized and the few H^+ ions present are replaced by Na^+ ions which are less mobile. But the product CH_3COONa^+ being a salt, is a strong electrolyte and it ionizes almost completely giving a large number of ions. Hence, from the beginning, the conductivity gradually increases instead of decreasing, as in the earlier case. After the equivalence point, excess of NaOH added gives fast moving OH^- ions and conductivity sharply increases. In the plot of conductance against volume of NaOH, two ascending lines, one steeper than the other is obtained and the volume of NaOH corresponding to the point at which these two curves meet gives the titre value. It must be plotted that the first end point will be that of hydrochloric acid (strong), while the second that of acetic acid (weak). The curve will be a combination of the two curves as given below.

PROCEDURE:

Prepare a standard solution of oxalic acid by dissolving 1.5750 of AR quality oxalic acid in 250ml of distilled water. Using this standardise the given NaOH soln. Dilute the given sample of acid mixture into 100 ml with distilled water. Pipette out 10ml of the sample into a beaker and add 10 ml of water Mix well. Insert the conductivity cell into the solution and measure the conductance. Add 0.2ml of 0.1N solution of NaOH, from the burette, into the mixture, stir well and measure the conductance of the solution. Similarly measure the conductance of the solution after every addition of 0.2 ml of 0.1 N NaOH, until a final volume of about 8.0ml of 0.1N NaOH is added.

Plot a graph between conductance and the volume of NaOH added and calculate the strength of HCl and CH_3 C00H in the given mixture.

OBSERVATION:

Weight of empty weighing bottle = W_1 = ____ g
Weight of bottle + Oxalic acid = W_2 = ____ g
Weight of bottle after transfer = W_3 = ____ g
Weight of oxalic acid taken = W_2 - W_3 = ____ g

Conc. of oxalic acid (x) = $\frac{(W_2 - W_3) \times 1000}{250 \times 63}$ = _____ N

TABLE - 1 STANDARDIZATION OF NaOH SOLUTION

Volume of oxalic acid = 25 ml.

S. No.	Burette Reading (ml)		Vol. of NaOH used (V_1) ml
	Initial	Final	
1			
2			
3			

Volume (V_1) =______ ml

TABLE-II CONDUCTOMETRIC TITRATION OF SAMPLE WITH NaOH

Volume of sample taken = 10 ml.

S.No.	Volume of NaOH added (ml)	Conductance (mS)	S.No	Volume of NaOH added (ml)	Conductance (mS)
1	0.0		22	4.2	
2	0.2		23	4.4	
3	0.4		24	4.6	
4	0.6		25	4.8	
5	0.8		26	5.0	
6	1.0		27	5.2	
7	1.2		28	5.4	
8	1.4		29	5.6	
9	1.6		30	5.8	
10	1.8		31	6.0	
11	2.0		32	6.2	
12	2.2		33	6.4	
13	2.4		34	6.6	
14	2.6		35	6.8	
15	2.8		36	7.0	
16	3.0		37	7.2	
17	3.2		38	7.4	
18	3.4		39	7.6	
19	3.6		40	7.8	
20	3.8		41	8.0	
21	4.0				

CALCULATION:

(a) CONCENTRATION OF NaOH

Vol. of oxalic acid taken = 25ml
Vol. of NaOH used = V_1 ml = ---------------- ml
Conc. of oxalic acid = x = ------------------N
Concentration of NaOH = N_1 =?
$25 \text{ X } x = V_1 \text{ X } N_1$
$\therefore N_1 = \frac{25x}{V_1} = y =$ ----------- = --------------N

$\therefore$ Conc. of NaOH = N_1 = --------------- N

(b) STRENGTHS OF HCl AND CH_3 COOH

From the graph

Vol. of NaOH consumed for HCl = V_a ml = -----------ml
Vol. of NaOH consumed for Acetic acid & HCl = V_b ml = ----------ml

(i) AMOUNT OF HCl IN THE MIXTURE:

Vol. of sample taken = 10 ml
Normality of NaOH = N_1 = --------- N
Normality of HCl = N_2 =-------------?
$10 \text{ x } N_2 = V_a \text{ x } N_1$

$N_2 = \frac{N_1 \times V_a}{10}$ = -------------- = -----------------N

Conc of HCl = N_2 = ------------- N

Amount of HCl in the whole of solution= W_{HCl} =

$= \frac{N_2 \times 36.5 \times 100}{1000}$ = --------------g

(ii) AMOUNT OF ACETIC ACID IN THE MIXTURE

Vol. of sample taken = 10 ml
Vol. of NaOH used for Acetic acid =V_b- V_a = ------ = ----------- ml
Normality of NaOH = N_1 = ----------------N
Normality of acetic acid = N_3 = -------?

10 x N_3 = (V_b- V_a) x N_1

$N_3 = \frac{(V_b - V_a) \times N_1}{10}$ = --------------- = ----------------N
Concentration of acetic acid = N_3 = -------------N

Amt. of CH_3 COOH in whole solution =

$$W_{CH_3COOH} = \frac{N_3 \times 60 \times 100}{1000} = \text{-----------g}$$

<u>RESULT</u>:

The amount of HCl in the given mixture was found to be = -----------g

The amount of CH_3 COOH in the given mixture was found to be= ---------g

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Internal Assessment:

Observation(5)	
Calculations, graph, result(10)	
Viva(5)	

EXPERIMENT NO. **DATE:**

DETERMINATION OF THE RATE CONSTANT OF ACID CATALYSED HYDROLYSIS OF AN ESTER

AIM:

To determine the rate constant of acid catalyzed hydrolysis of methyl acetate.

APPARATUS:

Thermostat, beakers, conical flasks, burettes, pipettes, etc.

THEORY:

A first order reaction is one in which the rate depends on concentration of only one of the reactants. Methyl acetate hydrolyses, in the presence of an acid, which acts as a catalyst, to give acetic acid and methyl alcohol.

$$CH_3COOCH_3 + H_2O \xrightarrow{\text{acid}} CH_3COOH + CH_3OH$$

The reaction velocity is given by

Rate = k' [CH_3COOCH_3] [H_2O], where k' is the specific reaction rate constant-(1)

Since water is present in large excess, its concentration remains practically constant throughout the reaction. As a result of this assumption, the above equation reduces to

Rate = k' [CH_3COOCH_3] where k' = k [H_2O] = constant----------(2)

Hence, the rate of reaction is determined by the first power of the concentration of the ester and so the reaction is of the first order. It is however, a pseudo first order reaction which is not first order but is forced to obey the first order rate expression. Such reactions involve more than one molecule in the chemical reaction. As acetic acid is produced during the hydrolysis of methyl acetate, the reaction can be followed by titrating the reaction mixture with standard solution of an alkali.

The value of k can be calculated according to the first order rate expression which is given by

$$k = \frac{2.303}{t} \times \log \frac{a}{a - x} \qquad \text{[or]}$$

$$k = \frac{2.303}{t} \times \log \frac{V_\infty - V_O}{V_\infty - V_t}$$

Where,
V_o = Volume of alkali used at t = 0 min,
V_t = Volume of alkali used at any time of reaction,
V_∞ = Volume of alkali used at the end of the reaction.

The values of rate constant can be calculated at different intervals of time t. It is independent of the initial concentration of the ester. It has the dimensions of time^{-1}.

PROCEDURE:

Take 100 ml of 0.5N HCl in a dry 250 ml conical flask and 10 ml of methyl acetate in a beaker. Place them separately in the thermostat, so as to reach an equilibrium temperature, for about 15 minutes. Fill the burette with 0.1N NaOH solution and take 3 conical flasks containing crushed ice. Transfer 10ml of methyl acetate into the conical flask containing 100ml of 0.5N HCl & start the stop clock. Shake the flask well and immediately withdraw 5ml of the reaction mixture, with the help of a pipette, into the conical flask with ice to arrest the reaction. Titrate this solution as rapidly as possible with 0.1N NaOH solution using phenolphthalein (5 drops) as an indicator. This titre value gives the amount of HCl in the reaction mixture at the start of the reaction. This is taken as V_O.

Repeat the above procedure of withdrawing 5ml of the reaction mixture adding into a conical flask containing crused ice and titrating with 0.1N NaOH at successive intervals of 5,10, 20,30,40,50, 60, 70, 80 and 90 minutes. These titre values are taken as respective V_t readings.

To find out the completion of hydrolysis of ester, transfer 25ml of the reaction mixture into a separate conical flask, cover it with a beaker inverted in a water bath and heat it for about 30 min at 70-80°C.

Pipette 5 ml of this mixture in to a conical flask and titrate against 0.1N NaOH using phenolphthalein (5 drops) as an indicator. The titre value represents the total amount of HCl and the amount of acetic acid formed at the end of reaction and is denoted by V_∞.

DETERMINATION OF THE RATE CONSTANT OF ACID CATALYSED HYDROLYSIS OF AN ESTER

OBSERVATION:

Room temperature =_______ ºC
Volume of 0.5 N HCl = 100 ml
Volume of ester = 10 ml

TABLE I :

TITRATION OF REACTION MIXTURE WITH 0.1N NaOH:

Volume of reaction mixture taken = 5 ml

S.No	Time (min)	Burette Reading		Volume of NaOH used V_t (ml)
		Initial	Final	
1	0			
2	5			
3	10			
4	20			
5	30			
6	40			
7	50			
8	60			
9	70			
10	80			
11	90			
12	∞			

CALCULATION:

The rate constant $$k = \frac{2.303}{t} \times \log\left(\frac{(V_\infty - V_O)}{(V_\infty - V_t)}\right)$$

where,

t = time of reaction in minutes,
V_O = Volume of NaOH required at start of reaction,
V_∞=Volume of NaOH required for the completion of reaction,
V_t = Volume of NaOH required at regular interval of time (t).

The value of **k** is obtained graphically by plotting graph of log $\frac{(V_\infty - V_O)}{(V_\infty - V_t)}$ against time `t'. The plot gives a straight line passing through origin with slope equal to k.

TABLE - II CALCULATION OF RATE CONSTANT (k)

Time in minutes (t)	**Volume of NaOH (V_t) m1**	$\log\left(\frac{(V_\infty - V_O)}{(V_\infty - V_t)}\right)$	$k = \frac{2.303}{t}\log\frac{(V_\infty - V_O)}{(V_\infty - V_t)}$ **(min^{-1})**
0			
5			
10			
20			
30			
40			
50			
60			
70			
80			
90			
∞			

Mean k = ----------------- min^{-1}

From the graph k = slope = $\frac{y_2 - y_1}{x_2 - x_1}$ = ---------------.

k = 2.303 x slope = ----------- min^{-1}

RESULT:

The rate constant of the acid catalyzed hydrolysis of methyl acetate at ---------°C was found to be

a) From the graph = _______ min^{-1}

b) By calculation = _______ min^{-1}

Internal Assessment:

Observation(5)	
Calculations, graph, result(10)	
Viva(5)	

EXPERIMENT NO. **DATE:**

ADSORPTION OF OXALIC ACID ON ACTIVATED CARBON

AIM:

To verify Freundlich adsorption isotherm by studying the adsorption of oxalic acid on activated carbon and to find the values of k and n.

APPARATUS:

Burettes, pipette, conical flasks, reagent bottles, shaking machine, funnel etc.

THEORY:

When a gas or particles in a liquid are equilibrated with a solid, they get concentrated on to the surface of the solid. This phenomenon of high concentrations of solute particles on the surface of the solid than on the bulk is called adsorption. The particles which gets adsorbed on the solid surface is known as adsorbate. The solid surface which adsorbs the particles is known as adsorbent. The adsorbent particles are held to the adsorbent either by physical forces (physisorption) or by chemical forces (chemisorption). The variation of extent of adsorption with concentration of the adsorbate at a fixed temperature is known as adsorption isotherm.

Adsorption of a solute from a solution onto a solid adsorbent is more difficult to treat theoretically than the corresponding adsorption of gases on solids. It appears, however, that in this case, too, like the gas-solid adsorption a monomolecular layer is formed. The solvating power of the solvent inhibits the formation of a multilayer.

For adsorption from solution, a commonly used isotherm is the Freundlich isotherm. If x is the mass of the solute adsorbed on mass m of adsorbent and c is the concentration of the solute in the solution, then the Freundlich isotherm is expressed as

$$x/m = a = kc^n \qquad \text{...... (1)}$$

where k and n are empirical constants. Taking log,

$$\log a = \log k + n \log c \qquad ..... (2)$$

This logarithmic form is convenient to use. If we plot log a versus log C the plot would be a straight line with slope equal to n and intercept equal to log k.

PROCEDURE:

Prepare 0.5 N (0.25m) solution of oxalic acid by dissolving 7.875g of oxalic acid in 250ml distilled water. Take five reagent bottles and number them one to five. Transfer through burette 10,20,30,40 and 50ml of 0.5 N oxalic acid solution. into each of these reagent bottle. Add 40,30,20,10 and 0 ml of water through a burette into each of these bottles to make the final volume equal to 50ml and mixed well. Add 5 g of activated carbon to the respective bottles and stopper each of them. Shake these bottles for about 45 minutes. The extent of adsorption depends on the equilibrium time. After shaking, allow the bottles to stand, to allow the particles to settle down. Filter the solutions of each bottle and collect the filtrate in separate bottles. Titrate 5ml liquids of the filtrate from each bottle with 0.1 N solution of sodium hydroxide using phenolphthalein indicator. Standardise NaOH solution by titrating with 5 ml of 0.5 N oxalic acid solution using phenolphthalein as a indicator. Calculate the value of k and n by a graph between log a and log Ce.

ADSORPTION OF OXALIC ACID ON ACTIVATED CARBON

OBSERVATION:

Weight of empty weighing bottle (w_1) = ------------------------g
Weight of bottle + oxalic acid (w_2) =-------------------------g
Weight of bottle after transfer (w_3) =------------------------ g
Weight of oxalic acid = (w_2-w_3)=--------------------------------g

Concentration of oxalic acid = $\frac{(w_2-w_3) \times 1000}{250 \times 63}$ = z = ----------N

STANDARDISATION OF SODIUM HYDROXIDE:

Volume of oxalic acid = V_1= 5.0 ml
Normality of Oxalic Acid = N_1= z = ---------------------N

S No.	**Burette Reading (ml)**		**Volume of NaOH (V_2) (ml)**
	Initial	**Final**	
1			
2			
3			

V_2 = ---------------ml.

Narmality of NaOH = N_2 =?

$N_1V_1 = N_2V_2$

$N_2 = \frac{N_1V_1}{V_2} = \frac{Z \times 5}{V_2} =$ = -------------------N

Therefore concentration of NaOH, N_2 = ------------------N

Room Temparature -------------°C

Mass of carbon = 5.0 g

S. No	Vol. of oxalic acid (V)	Vol. of water added (ml)	Initial conc. of oxalic acid Ci=ZxV /50	Vol. of N_2 normal NaOH (Vi) (ml)	Conc. Of oxalic acid Ce=N_2x Vi/5	Conc of oxalic acid adsorbed (Ci -Ce)	Moles of oxalic acid adsor-bed $\frac{C_i - C_e}{20}$ =n	Mass of oxalic acid adsorbed x=nx63 (g)	Extent of adsorption a= x/m =x/5	Log Ce	Log a
1	10	40									
2	20	30									
3	30	20									
4	40	10									
5	50	0									

Plot a (x/m) Vs Ce
Plot log a Vs log Ce,

From the 2nd plot of log **a** Vs log **Ce**
Intercept log k = y = slope = n = ----------

K = log y = --------------- = -------------------.

RESULT:

The Frendlich adsorption isotherm was verified for the adsorption of oxalic acid on activated carbon.

The value of **k** was found to be _______

The value of **n** was found to be _______

Internal Assessment:

Observation(5)	
Calculations, graph, result(10)	
Viva(5)	

EXPERIMENT NO. **DATE:**

PHASE DIAGRAM OF THREE COMPONENT SYSTEM

AIM:

To draw the phase diagram of three component (water-chloroform-acetic acid) system.

APPARATUS:

Test tube, Burette, Reagent bottles.

THEORY:

The phase rule states that, for a heterogeneous system at equilibrium, the sum of number of phases (P) and the degrees of freedom (F) is greater than the number of components (C) by two.

$P + F = C + 2$

$\Rightarrow \mathbf{F = C - P + 2}$

For a three component system, C = 3

Therefore, $F = 3 - P + 2 \Rightarrow F = 5 - P$

For a system containing one phase (P = 1)

$F = 5 - 1 = 4$

Hence the phase diagram should illustrate four variables which is difficult. Thus fixing pressure and temperature constant for a three component system, the phase rule reduces to F = 3 - P. A triangular graph is used to describe the ternary system in terms of the remaining variables –two of the three concentrations.

The simplest three components are those in which a liquid system breaks down into two phases. The system CH_3COOH-$CHCl_3$-H_2O is such a system over a certain temperature range. A two phase region occurs in systems with relatively low amounts of acetic acid. The tie lines passing through the two phase region join the compositions of the two phases that are in equilibrium.

PROCEDURE:

Take three burettes. Fill each of them respectively with water, chloroform and acetic acid. Into a test tube add 10 ml of chloroform from the burette. Now add 1 ml of water and mix until two layers are formed. Now add acetic acid until the two layers merge to become a single homogeneous layer. Note down the value of acetic acid. Add 1 ml of water in the test tube and repeat the addition of acetic acid dropwise. Repeat this process after each 1 ml addition of water until the volume of water reaches 10 ml. Take another test tube and add 10 ml of water and 1 ml of chloroform; add acetic acid dropwise from the burette until the two layers merge into a homogeneous layer. Repeat this process after each addition of 1 ml of chloroform until its volume reaches 9.0 ml. From these values, calculate the respective volume percentage of the three components and plot the phase diagram in the graph.

OBSERVATION:

PHASE DIAGRAM OF THREE COMPONENT SYSTEM:

Sl. No	Volume of			Volume %		
	$CHCl_3$ V_1(ml)	H_2O V_2(ml)	CH_3COOH V_3(ml)	$CHCl_3$ $V_1/(V_1+V_2+V_3)$	H_2O $V_2/(V_1+V_2+V_3)$	CH_3COOH $V_3/(V_1+v_2+V_3)$
1.	5.0	0.5				
2.	5.0	1				
3.	5.0	1.5				
4.	5.0	2				
5.	5.0	2.5				
6.	5.0	3				
7.	5.0	3.5				
8.	5.0	4				
9.	5.0	4.5				
10.	5.0	5				
11.	5.0	5.5				
12.	5.0	6				
13.	5.0	6.5				
14.	5.0	7				
15.	5.0	7.5				
16.	5.0	8				

17.	5.0	8.5				
18.	5.0	9				
19.	5.0	9.5				
20.	10	10				
21.	9.5	5.0				
22.	9	5.0				
23.	8.5	5.0				
24.	8	5.0				
25.	7.5	5.0				
26.	7	5.0				
27.	6.5	5.0				
28.	6	5.0				
29.	5.5	5.0				
30.	5	5.0				
31.	4.5	5.0				
32.	4	5.0				
33.	3.5	5.0				
34.	3	5.0				
35.	2.5	5.0				
36.	2	5.0				
37.	1.5	5.0				
38.	1	5.0				
39.	0.5	5.0				
40.	0	5.0				

Plot the phase diagram.

From the plot, the composition of the given mixture was found to be

- $CHCl_3$ = --------------------- % by volume,
- H_2O = --------------------- % by volume,
- CH_3COOH = -------------------- % by volume.

RESULT:

The phase diagram for $CHCl_3$ – H_2O – CH_3COOH system was plotted.

The composition of the three components in the given mixture was found to be

- $CHCl_3$ = --------------------- % by volume,
- H_2O = --------------------- % by volume,
- CH_3COOH = -------------------- % by volume.

Internal Assessment:

Observation(5)	
Calculations, graph, result(10)	
Viva(5)	

EXPERIMENT NO. DATE:

DETERMINATION OF MOLECULAR WEIGHT BY RAST METHOD

AIM:

a) To determine the molal depression constant of naphthalene using diphenylamine as solute.

b) To find out the molecular weight of the given compound using the value of molal depression constant.

APPARATUS:

Hot water bath, glass tube, thermometer, weighing bottles, etc.

THEORY:

The depression in freezing point of a solvent is a colligative property of dilute solution of a non-volatile solute in a volatile solvent. A colligative property is defined as that property which depends upon the composition of the solute (number of particles of solute) and not on the nature of solute.

When a non-volatile solute is dissolved in a volatile solvent, there occurs a depression in the freezing point of the solvent. This depression in freezing point of the solvent is given by the expression

$$\Delta T_f = k_f \times m.$$

where ΔT_f = depression in freezing point

k_f = molal depression constant

m = molality

Molality is given by

$$m = \frac{w_2}{M_2 \times w_1} \times 1000$$

where w_2 = weight of solute in grams

w_1 = weight of solvent in grams

M_2 = molal mass of solute

Thus $\Delta T_f = k_f\left(\frac{w_2}{M_2 \times w_1} \times 1000\right)$

The molal depression constant (k_f) is thus defined as that value of depression in freezing point which may be theoretically obtained for 1 molal solution.

k_f can be experimentally determined, by determining ΔT_f using a solute of known molal mass (M_2) using the expression

$$k_f = \frac{M_2 \times w_1 \times \Delta T_f}{w_2 \times 1000}$$

Using the above value of k_f, the molal mass of unknown sample can be obtained using the expression

$$M_2 = \frac{k_f \times w_2 \times 1000}{w_1 \times \Delta T_f}$$

PROCEDURE:

Take accurately 2.0000 g of pure naphthalene in a clean dry glass tube. Heat the tube in a constant heating water bath and determine the freezing point. Add about 0.2 g of diphenylamine into the tube and once again determine the freezing point. Repeat the above procedure after adding another 0.2 g of diphenylamine. Calculate the molal depression constant for naphthalene. Repeat the above procedure with 2.0000g of naphthalene and 0.2 & 0.4 g of unknown compound to determine its molecular weight.

<u>OBSERVATION</u>:

DETERMINATION OF MOLECULAR WEIGHT BY RAST METHOD

(A) MOLAL DEPRESSION CONSTANT

Sl. No	Weight of Naphthalene w_1 (g)	Weight of Diphenylamine w_2 (g)	Melting point (°C)	Freezing point (°C)	Mean Freezing point (°C)	$k_f = \frac{169.22 \times w_1 \times \Delta T_f}{w_2 \times 1000}$
1		0.0000				
2		0.2000				
3		0.4000				

Mean k_f = ------ g °C mol^{-1}

(B) MOLECULAR WEIGHT OF UNKNOWN COMPOUND

Sl. No	Weight of Naphthalene w_1 (g)	Weight of unknown compound w_2 (g)	Melting point (°C)	Freezing point (°C)	Mean Freezing point (°C)	$M_2 = \frac{k_f \times w_2 \times 1000}{w_1 \times \Delta T_f}$
1		0.0000				
2		0.2000				
3		0.4000				

Mean = ------ g mol^{-1}

CALCULATION:

(A) k_f OF THE SOLVENT

Weight of the solvent taken = w_1 g
Weight of the solute = w_2 g
Molecular weight of the solute, diphenylamine (M_2) = 169.22 g/mol
Freezing point of solvent = T_A °C
Freezing point of solvent after addition of solute = T_B °C
Depression in freezing point, ΔT_f = $(T_A - T_B)$ °C
Molal depression constant $$k_f = \frac{169.22 \times w_1 \times \Delta T_f}{w_2 \times 1000}$$

(B) MOLECULAR WEIGHT:

Weight of the solvent taken = w_1 g
Weight of the solute = w_2 g
Freezing point of the solvent = T_A °C
Freezing point of the solvent after addition of solute = T_B °C
Depression in freezing point ΔT_f = $(T_A - T_B)$ °C
Molecular weight of the solute $$M_2 = \frac{k_f \times w_2 \times 1000}{w_1 \times \Delta T_f}$$

RESULT:

The molal depression constant of naphthalene and the molecular weight of the unknown compound were determined and the results are as follows:

Set. No.	k_f (g °C mol^{-1})	Molecular weight (g mol^{-1})
1		
2		
Mean		

Internal Assessment:

Observation(5)	
Calculations, graph, result(10)	
Viva(5)	

EXPERIMENT NO. **DATE:**

DETERMINATION OF RATE CONSTANT OF ALKALINE HYDROLYSIS OF AN ESTER

AIM:

To determine the rate constant of alkaline hydrolysis of ethyl acetate using sodium hydroxide

APPARATUS:

Burettes, pipettes, conical flask, magnetic stirrer, reagent bottles etc.

THEORY:

The alkaline hydrolysis of an ester, such as ethyl acetate by sodium hydroxide follows a second order kinetics. The reaction can be represented as follows.

$$CH_3COOC_2H_5 + NaOH \text{ ------> } CH_3COONa + C_2H_5OH$$

The rate expression for the above reaction can be represented as follows.

rate = k [$CH_3COOC_2H_5$] [NaOH], where k = specific reaction rate constant of the reaction.

It can be seen that the rate of the reaction is first order with respect to both the reactants. The integrated rate expression for the reaction can be represented as

$$k = \frac{2.303}{t(b-a)} \log \frac{b(a-x)}{a(b-x)}$$

where ‘a’ and ‘b’ are the initial concentration of the ester and sodium hydroxide respectively and b is greater than a.

The reaction rate constant can be experimentally determined by transferring suitable aliquots of reaction mixture, at regular intervals, into acetic acid solution and titrating the acid with base. The magnitude of ‘k’ can be calculated using the formula.

$$kt = \frac{2.303 \times 10}{N(V - V_\infty)} \log \frac{(V_\infty - V_o)(V - V_t)}{(V - V_o)(V_\infty - V_t)}$$

where

V_o = Volume of base required at the start of reaction
V_t = Volume of base required at any time during the reaction
V_∞ = Volume of base required at the end of the reaction
V = Volume of base required for acetic acid
N = Normality of base used for titration
t = Time of the reaction

PROCEDURE:

Prepare a 0.05 N solution of oxalic acid by dissolving 0.7875 g of AR quality of oxalic acid in 250ml of distilled water. Standardize the given solution of barium hydroxide with oxalic acid solution by titrating 25 ml of oxalic acid with barium hydroxide solution, using phenolphthalein as the indicator. Place 50 ml each of 0.05 N solution of ethyl acetate and 0.03 N solution of sodium hydroxide in two separate conical flasks. Place these two conical flasks in a water bath for about 15-20 min to attain the room temperature. Take six conical flasks and pipette out 10 ml of 0.05 N solution of acetic acid into each of them. Transfer the solution of sodium hydroxide into the ester solution, stir the mixture using magnetic stirrer and start the stop clock. At time intervals of 2, 4, 6, 8, 10 and 12 minutes from the start of the reaction, pipette out 10 ml aliquots of the reaction mixture into each of the six conical flasks containing 10 ml of N/20 acetic acid solution, in order to arrest the reaction. Titrate the above acetic acid solution with N/20 barium hydroxide, using phenolphthalein as indicator. The titre value gives the value of V_t.

Heat the remaining reaction mixture in a water bath, maintained at 70-80°C, for about half an hour to complete the reaction. Cool the reaction mixture and transfer 10 ml of this mixture into a conical flask containing 10 ml of N/20 acetic acid solution. Titrate the above solution with N/20 barium hydroxide solution using phenolphthalein as an indicator. The titre value gives V_∞.

Pipette out 5.0 ml of 0.03N sodium hydroxide solution into a conical flask containing 10ml of N/20 acetic acid soln. Titrate this mixture with N/20 barium hydroxide solution using phenolphthalein as the indicator. The titre value represents V_o.

Titrate 10 ml of N/20 acetic acid with N/20 barium hydroxide using phenolphthalein as a indicator. The titre value represents V.

Calculate the value of rate constant with the help of these observations.

RATE CONSTANT OF ALKALINE HYDROLYSIS OF AN ESTER

OBSERVATION:

- Weight of empty weighing bottle = w_1 = ___________g
- Weight of bottle + oxalic acid = w_2 = ______________g
- Weight of bottle after transfer = w_3 = ______________g
- weight of oxalic acid = $w_2 - w_3$ = _________________g
- Concentration of oxalic acid = $\frac{(w_2 - w_3)\times 1000}{250\times 63}$ = ______ N

STANDARDIZATION OF BARIUM HYDROXIDE:

Volume of oxalic acid V_1= 25ml
Concentration of oxalic acid = N_1 = -------------------N

S. No.	Burette Reading (ml)		Volume of Ba(OH)$_2$ used V$_2$ (ml)
	Initial	Final	
1			
2			
3			

V_2 =-------------ml

Concentration of barium hydroxide = N_2 =---------------?

$N_1V_1 = N_2V_2$

$N_2 = \frac{N_1V_1}{V_2} = \frac{N_1\times 25}{V_2}$ = ----------------N

RATE CONSTANT OF REACTION:

S. No.	Time (min)	Burette reading (ml)		Volume of $Ba(OH)_2$ used (ml)	$\log\frac{(V_\infty - V_o)(V - V_t)}{(V - V_o)(V_\infty - V_t)}$	$kt = \frac{2.303\times 10}{N(V - V_\infty)}\times$ $\log\frac{(V_\infty - V_o)(V - V_t)}{(V - V_o)(V_\infty - V_t)}$	$k = \frac{kt}{t}$ $l\ mol^{-1}\min^{-1}$
		Initial	Final				
1	2						
2	4						
3	6						
4	8						
5	10						
6	12						
7							

Mean k = -------l $mol^{-1}min^{-1}$

V = _______ ml
V_o = ______ ml
V_∞ = ______ ml

CALCULATION:

$$kt = \frac{2.303\times 10}{N(V - V_\infty)}\log\frac{(V_\infty - V_o)(V - V_t)}{(V - V_o)(V_\infty - V_t)}$$

V = Volume of $Ba(OH)_2$ required for titration of acetic acid.

V_o = Volume of $Ba(OH)_2$ used required at the start of reaction.

V_∞=Volume of $Ba(OH)_2$ required at the completion of reaction.

V_t = Volume of $Ba(OH)_2$ required during the course of reaction.

N = Normality of the $Ba(OH)_2$ soln.

Plot ,

$$kt = \frac{2.303 \times 10}{N(V - V_\infty)} \log \frac{(V_\infty - V_o)(V - V_t)}{(V - V_o)(V_\infty - V_t)}$$

Against ‘ t ‘

From the plot, Slope = k = = ------------- l $mol^{-1}min^{-1}$

RESULT:

The rate constant of the alkaline hydrolysis of ethyl acetate was determined at ____ ˚C and was found to be

a) by graph ______l mol^{-1} min^{-1}

b) by calculation ______ l mol^{-1} min^{-1}

Internal Assessment:

Observation(5)	
Calculations, graph, result(10)	
Viva(5)	

EXPERIMENT NO. **DATE:**

PARTITION COEFFICIENT OF BENZOIC ACID BETWEEN BENZENE AND WATER

AIM:

To find out the partition coefficient of benzoic acid between benzene and water.

APPARATUS:

Reagent bottles, burette, pipette, conical flask, separating funnel, shaking machine etc.

THEORY:

If the solute has the same molecular weight in both the immiscible solvents, i.e., it is in the same molecular state, then its partition coefficient K, between the two layers will be given by,

$$K = C_A/C_B \text{ --------------- (i)}$$

where C_A and C_B are the respective concentrations of the solute in the two solvents. Suppose in the solvent A, the solute has the normal molecular weight, while in the second solvent B, it is associated as follows

$$nx\text{----------->} \quad X_n$$

In such a case, the ratio C_A / C_B will not be constant. The value of partition coefficient can now be calculated as follows.

Let C_1 be the concentration of the solute [x] in phase I (solvent A) and C_2 be the total concentration in phase II (second solvent B). In phase II, the solute is associated and it exists in equilibrium with unassociated molecule.

$$\text{(i.e) } nx\text{----------->} X_n$$

equilibrium constant $k_{eq} = \frac{[x]^n}{[X_n]}$ -------(ii)

If the solute exists largely as associated molecules which is generally true except at large dilutions, the concentration of the associated molecule $[(X)_n]$ may be taken as equal to C_2.

The total concentration of X = $[(x)n]$ = C_2 ----------(iii)

From equation (ii) and (iii) $(k_{eq}$ x C) 1/n= Constant x $(C_2)^{1/n}$ ----------- (iv)

As the distribution law is valid only when concentrations of similar molecular species in the two solvents are taken into consideration, therefore

$C_{1/}\,[X] = \text{Constant}$

Substituting for [x]

$C_1 / n\sqrt{C_2}$ = Constant = K (partition coefficient)

In case of benzoic acid which generally exists as dimer in aprotic solvents, the value of n = 2. $K = C_1 / \sqrt{C_2}$

PROCEDURE:

Take three reagent bottles and mark them as 1, 2, and 3. Add 50ml of benzene and 50 ml of water into each of the 3 reagent bottles. Add 0.5, 1.0, 1.5 g of benzoic acid into bottle numbers 1, 2, and 3 respectively. Stopper the bottles properly and shake all the bottles for about 30-45 minutes in a shaking machine. Allow the mixture to separate into two layers, the lower layer will be the aqueous layer, while the upper layer will be the benzene layer.

Take 5 ml of the benzene layer, from each bottle by means of a pipette in a conical flask. Add 4-5 drops of phenolphthalein indicator. Titrate it against 0.1N NaOH solution. Repeat the process till you get two concordant readings. Similarly titrate the benzene layer of each of the other two bottles by pipetting out 5 ml of the solution and titrating it against 0.1 N NaOH solution using 4-5 drops of phenolphthalein. Pipette out 5 ml of the aqueous layer of the first bottle and titrate it against 0.01N NaOH solution, using phenolphthalein (4-5 drops) as the indicator. Repeat the process for the other bottles also.

PARTITION COEFFICIENT OF BENZOIC ACID BETWEEN BENZENE AND WATER

OBSERVATION

Room temperature =   °C

TABLE I: TITRATION OF AQUEOUS LAYER WITH 0.01N NaOH SOLUTION

Volume of water layer = 5.0 ml

Bottle No.	Burette Reading (ml)		Volume of 0.01N NaOH solution (V_1 ml)
	Initial	Final	
I			
II			
III			

TABLE II: TITRATION OF BENZENE LAYER WITH 0.1N NaOH SOLUTION

Volume of benzene layer = 5.0 ml.

Bottle No.	Burette Reading (ml)		Volume of 0.1N NaOH solution (V_1 ml)
	Initial	Final	
I			
II			
III			

CALCULATIONS:

TABLE III: CONCENTRATION OF BENZOIC ACID IN AQUEOUS LAYER (C_1)

Volume of water layer = 5.0 ml

Bottle No.	Vol. of 0.01N NaOH used (V_1 / ml)	Normality of benzoic acid $N_1 = \frac{V_1 X 0.01}{5}$	Concentration of benzoic acid $C_1 = N_1 X 122$ (g /l)
I			
II			
III			

TABLE IV : CONCENTRATION OF BENZOIC ACID IN BENZENE LAYER (C_2)

Volume of benzene layer = 5.0 ml

Bottle No.	Vol. of 0.1N NaOH used (V_2 / ml)	Normality of benzoic acid $N_2 = \frac{V_2 X 0.1}{5}$	Concentration of benzoic acid $C_2 = N_2 X 122$ (g /l)
I			
II			
III			

TABLE V: CALCULATION OF PARTITION COEFFICIENT

Bottle no.	Conentration of benzoic acid in water layer, C_1 (g/l)	Concentration of benzoic acid in benzene layer, C_2 (g/l)	$K = \frac{C_1}{(C_2)^{1/2}}$
I			
II			
III			

Mean K = ----------------

<u>RESULT</u>:

The partition coefficient of benzoic acid between water and benzene at ______°C was found to be -----------------.

Internal Assessment:

Observation(5)	
Calculations, graph, result(10)	
Viva(5)	